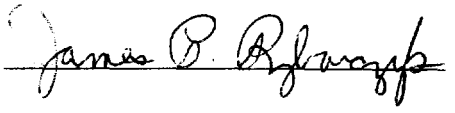
LEAD LEACHING FROM DRINKING FOUNTAIN WATER SUPPLIES

AN HONORS THESIS (HONRS 499)

by

Kristie L. Senter

Dr. James P. Rybarczyk



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For the past several decades, lead (Pb) hazards in our environment have been the focus of much scientific interest. Efforts have been made to identify and minimize its sources. These lead sources can be found just about anywhere. The Environmental Protection Agency has found this potentially toxic lead to contaminate through the air, dust, food, gasoline, and peeling paint. Recently drinking water supplies have been targeted with significantly lower lead limits, showing particular emphasis on older dwellings and schools. Bill Morgan, the Ball State University Environmental Officer, brought this potential hazard to the attention of the Chemistry Department's analytical research team at Ball State University. Due to the impact that lead toxins have on young children, we decided to look at the presence of lead in the drinking water of a controlled scholastic environment. This study monitored lead and other heavy metals in a fairly large population of academic drinking water coolers. In addition to monitoring lead levels, kinetic studies were conducted to determine the effectiveness of flushing the systems.

Focusing particularly on the impact that lead has on the body, it is known that in the blood, lead has a half-life of thirty days. Nevertheless, it seems that the more complex the tissue, the longer the retention of lead (ie. the brain). The adult skeleton can store lead for more than ten years. Essentially, the problem seems to start with absorption rather than retention. There are two methods for the absorption of lead. One method is the gastrointestinal absorption, in which the majority of the lead is

not absorbed. Instead, it is passed through the faeces. The other method is pulmonary absorption. This route has the possibility of having a greater uptake of approximately 40 percent. Ultimately, it is important to consider the solubility of lead when determining its absorption. A large chunk of lead is less likely to be absorbed due to its lack of solubility. It is much more easily absorbed when broken down, as in the case of lead dissolving in water. In addition, age is a determinant of absorption also. The younger the individual, the more retention and absorption that individual may encounter. It is even possible to cause brain damage in children with large exposures to lead. Overall physical and mental development and functioning in children can be affected with even lower exposures. Here in lies the reason why this study took place in a scholastic environment: we wanted to understand and be aware the dangers to which we could possibly exposing young people.(Lansdown and Yule, 1986)

Within this study, thirty-three Ball State University campus buildings were sampled in a one month time frame. These buildings were divided into five geographic sectors, yielding three hundred and fifty total water samples. Important preliminary results showed no correlation between high lead levels and geographic sectors or by buildings. The high lead levels appeared to be random and not caused by the old 1800's underground campus waterpipe distribution or by the individual building plumbing. Therefore, since it seemed to be a random process, it was probably concentrated in the water coolers.

The strict sample protocol consisted of sampling the old model

Halsy/Taylor electric chill water coolers. These coolers were specifically targeted due to their construction with lead alloy solder and actual lead piping components. The age of these coolers spanned from the installation of the Practical Arts building in 1953, the Health Center in 1963, the Cooper Science building in 1967, and the Architecture building in 1983. Standard survey samples of 100ml from the initial use of the fountain (ie no purging) were collected in Nalgene bottles which were previously rinsed with deionized water. The pH and conductivity measurements were both conducted within one hour of sampling. Then each water sample was preserved with 250ul of trace metal analysis purity HNO_3. A blank of 100ml of 2 umho deionized water was also preserved with HNO_3 and run with each group of samples. For the kinetics experiments, only 10ml of water samples were obtained in Nalgene bottles and preserved by 10ul of HNO_3.

Specifically focusing on the analytical analysis, the pH was conducted within one hour of sampling on a Orion Research Digital Ionanalyzer/501 and a Corning pH combination electrode. The pH meter was calibrated on pH= 4.00 and 7.00 buffers. Conductivity was measured within one hour of sampling on YSI Conductance/Resistance Meter, YSI Model 34, with a dip cell constant of K=100 + 2%. After the HNO_3 preservation, the trace metal analysis, being the heart of the study, was usually conducted within twelve hours of sampling. Fisher Atomic Absorption standards (1000ppm) were used to prepare a set of five standards for each element (5, 10, 25, 50, 100ppb). A blank and these five standards were run at the beginning of each analysis run.

Meanwhile, at least two standards were placed intermittently along with the fountain samples in order to supervise the quality and consistency of the graphite tubes. Beer's Law plots and linear equations were utilized for each analysis run. Typical linearity was at 99.99% or better and if there were any deviations, the standards were remade.

Besides testing for lead, we also looked at some other elements or conditions that could have been involved in the plumbing. The chart below shows the results of these tests. None of these elements or conditions showed any correlation with lead.

NONE OF THESE ELEMENTS OR CONDITIONS SHOWED ANY CORRELATION WITH Pb

	Fe	Cr	Ni	Cd	Na	pH	Cond.
High	214ppb	8ppb	12ppb	17ppb	29ppm	9.13	1750 umho
Low	<2ppb	<2ppb	<2ppb	<2ppb	7ppm	7.29	900 umho
Avg	66ppb	4ppb	3ppb	4ppb	11ppm	7.91	1275 umho
Detect Limits	6% below	50% below	63% below	19% below	----	----	----

*** Using the Pb samples which were over 10ppb, 50% of the Na tests were on the High and Low sides of the Average.**

**** The most common pH = 7.80 - 8.00 (38% of the samples). Of the Pb samples over 10ppb, 42% of pH were below the Average; 58% were above.**

***** Of the Pb samples over 10ppb, all conductivity tests were closely grouped on either side of the Average.**

Many of these elements had a good portion of their samples registering below the detection limits. Using the lead samples which were 10ppb or over, all these elements seemed to be grouped about the mean. In turn, we assume no correlation with lead among

these elements.

Nevertheless, two more elements did seem to show a correlation with lead. Of the high lead level samples, an overwhelming 95% showed a high Zinc level also. Meanwhile, in this same high lead level sampling, only 5% with a low Zinc level occurred.

CLOSELY ASSOCIATED WITH Pb LEVELS

	Zn	Cu
HIGH	**2,711 ppb**	**2,461 ppb**
LOW	**2 ppb**	**3 ppb**
AVERAGE	**124 ppb**	**181 ppb**
1ST HALF OF SAMPLES	**45 ppb Zn and 2.5 ppb Pb**	**81 ppb Cu and 3.48 ppb Pb**
%OF 1ST HALF OVER 10ppb Pb	**5%**	**21%**
2nd HALF OF SAMPLES	**438 ppb Zn and 7.1 ppb Pb**	**722 ppb Cu and 5.94 ppb Pb**
%OF 2nd HALF OVER 10 ppb Pb	**95%**	**79%**

We also see the same type of trend with the Copper.

For the trace metal instrumentation, the Perkin Elmer Model 5500 Spectrophotometer was used in the conventional mode in combination with the Perkin Elmer HGA 500 Graphite Furnace. This instrumentation analysis required pyrolytically coated tubes. Ultimately, the Na analysis was run on a Plasma Therm 90 ICP Ar plasma emission source. Here the normal mode was required for operation. Precision for the graphite furnace was typically 2.9%

relative standard deviation. For the Inductively Coupled Plasma, precision was 4-5%. The following table shows a list of elements, their wavelengths, and their detection limits which were analyzed. (These detection limits were three times the standard deviation of the background. The background was measured for each of these using a thousand samples.)

TRACE METAL INSTRUMENTATION-

Element	λ , nm	DL (3σ)
Pb	283.3	2ppb
Cr	357.9	2ppb
Ni	232.2	2ppb
Cu	324.9	2ppb
Fe	248.6	1ppb
Zn	214.1	5ppb
Na	589.0	ICP not measured

Each individual sample was analyzed in triplicate, with precision typically in the 2-5% range. Occasionally, a sample precision reached 12%, but was then reanalyzed.

Each individual sample was analyzed in triplicate, with precision typically in the 2-5% range. Occasionally, a sample precision reached 12%, but was then reanalyzed. Due to Zinc's horrendous background, it was very difficult to analyze. On the other hand, Sodium was at such a high level that we did not need to test further.

When this study began, the Federal Drinking Water Limit was 50ppb. This was recently lowered in 1991 to 20ppb. For water cooler replacement, our target area of concern was Pb levels at

10ppb and above. Looking at the following Pb level distribution table, the highest level we found was at 122ppb. The lowest Pb level was below the detection limits, while the average was at 4ppb.

WHEN STUDY BEGAN, FEDERAL DRINKING WATER LIMIT WAS 50 ppb. THIS WAS LOWERED IN 1991 TO 20ppb.

Pb LEVEL DISTRIBUTION
HIGH = 122ppb LOW = <2ppb AVG = 4ppb
<2ppb = 31.1%
2.0-2.9 = 16.7%
3.0-3.9 = 10.6%
4.0-4.9 = 5.6%
5.0-5.9 = 7.6%
6.0-6.9 = 5.0%
7.0-7.9 = 2.5%
8.0-8.9 = 3.5%
9.0-9.9 = 2.0%
10-19 = 10.6%
20-29 = 1.5%
30-39 = 1.5%
>40 = 1.5%

*** 15.1% OR 1 IN 6 FOUNTAINS ARE IN THE AREA OF CONCERN FOR REPLACEMENT**

The shaded region represents our area of concern. This means 15.1% or one in six water coolers fall into this category for possible replacement. In essence, this hazard is not a major problem at Ball State University.

From here, we decided to look at one large building complex and sample the thirty water coolers during peak midweek usage. Breaking the building up into three sections and five floors was pertinent in order to see if the location within the building had any bearing on the lead levels.

Survey of 30 Fountains in One Large Building Complex
April 1991 at Peak Midweek Usage

	WEST WING	CENTER	EAST WING
	Pb, ppb	Pb, ppb	Pb, ppb
GROUND	3	<2	<2
	<2	----	6
	----	----	2
FLOOR 1	<2	none	<2
	<2	----	----
FLOOR 2	<2	4	<2
	<2	2	7
	----	----	19
FLOOR 3	<2	<2	4
	<2	2	12
FLOOR 4	<2	8	<2
	<2	<2	<2
	----	2	----
	----	7	----

Looking at the table above, one can see the majority of the coolers registered below the detection limits. Once again, this does not seem to indicate a major problem.

Meanwhile, this lead us to look at the amount of usage the fountains were receiving within the same building. Peak usage

tended to run during the middle of the semester, middle of the week, and middle of the day. Minimal usage was surveyed during the end of the year break on a Monday morning. The building was generally deserted all weekend and therefore not much fountain usage occured. During the first summer session in the middle of the week at eight o'clock a.m., the moderate usage was determined.

Comparison of Pb Levels at Peak, Minimal, and Moderate Usage

(all ppb, Pb)

	Peak	Minimal	Moderate
CP-11	**<2**	**16**	**----**
CP-52	**6**	**28**	**15**
CP-92	**2**	**21**	**6**
CP-253	**19**	**19**	**5**
CN-215	**4**	**15**	**<2**
CP-409	**<2**	**4**	**----**
Peak Usage= 4-11-91 mid semester, mid week, mid day			
Minimal Usage= 5-6-91 end of year break; Monday 7AM			
Moderate Usage= 5-15-91 1st summer session, mid week 8AM			

One can easily detect a slight fluxuation in relation to usage. For example, at peak usage site CP-52 shows 6ppb. In contrast, the minimal usage for the same site rose to 28ppb of lead. At 15ppb we found the moderate usage. Here a waving pattern becomes apparent.

Looking at some of the other buildings and targeting the highest lead level sites, usage seemed to be a factor in lead concentration once again. Taking a closer look at the Practical Arts Building,

one can see that at minimal usage during the summer break, the lead level ran 120ppb. Then on a midmorning Monday of the first summer session, the level dropped below detection limits. Over the weekend the water cooler received little usage and the lead level had time to climb to 13ppb by early morning Monday. Two days later, under midweek/midmorning usage, the lead levels fell to 9ppb. Again we see variability due to usage of the coolers.

Highest Lead Level Site
Variability as a Function of Usage
(all ppb, Pb)

	Summer Break	1st Summer Session	1st Summer Session	1st Summer Session
	7 AM Monday	10 AM Monday	7 AM Monday	10 AM Wednesday
Health Center	122	17	39	38
	125	31	80	44
Pratical Arts	120	<2	13	9
	16	<2	15	11
	27	17	29	25
Elliot Hall	28	11	29	20
Business	16	<2	24	3

The next step was to get an idea of the lead dosage people actually receive when they drink from these water coolers. We monitored one fountain on three different Spring days and kept track of the number of people using the coolers while timing each individual drink. The wide range in the climatic temperatures was noted in order to see if drink time would vary with the outside temperature. A trend did appear which suggested that as the

temperature increased, the drink time increased.

	AVERAGE DRINK		
TEMP.	**30° F**	**48° F**	**63° F**
# OF SUBJECTS PER HR.	**30**	**39**	**39**
TIMED DRINK	**1.78 (sec) ± 1.19 (sec)**	**1.86 (sec) ± 1.39 (sec)**	**2.97 (sec) ± 2.07 (sec)**
HIGH	**4.34 sec**	**6.46 sec**	**7.87 sec**
LOW	**.52 sec**	**.58 sec**	**.40 sec**

By finding the average fountain flow to be approximately 40 mL per second, the drink volume was then easily calculated.

AVERAGE FOUNTAIN FLOW = 40ml/sec			
DRINK VOLUME	**71.12 ml ± 47.84 ml**	**74.36 ml ± 55.44 ml**	**118.5 ml ± 82.96 ml**
HIGH	**173.6 ml**	**258.4 ml**	**314.8 ml**
LOW	**20.8 ml**	**23.2 ml**	**16 ml**

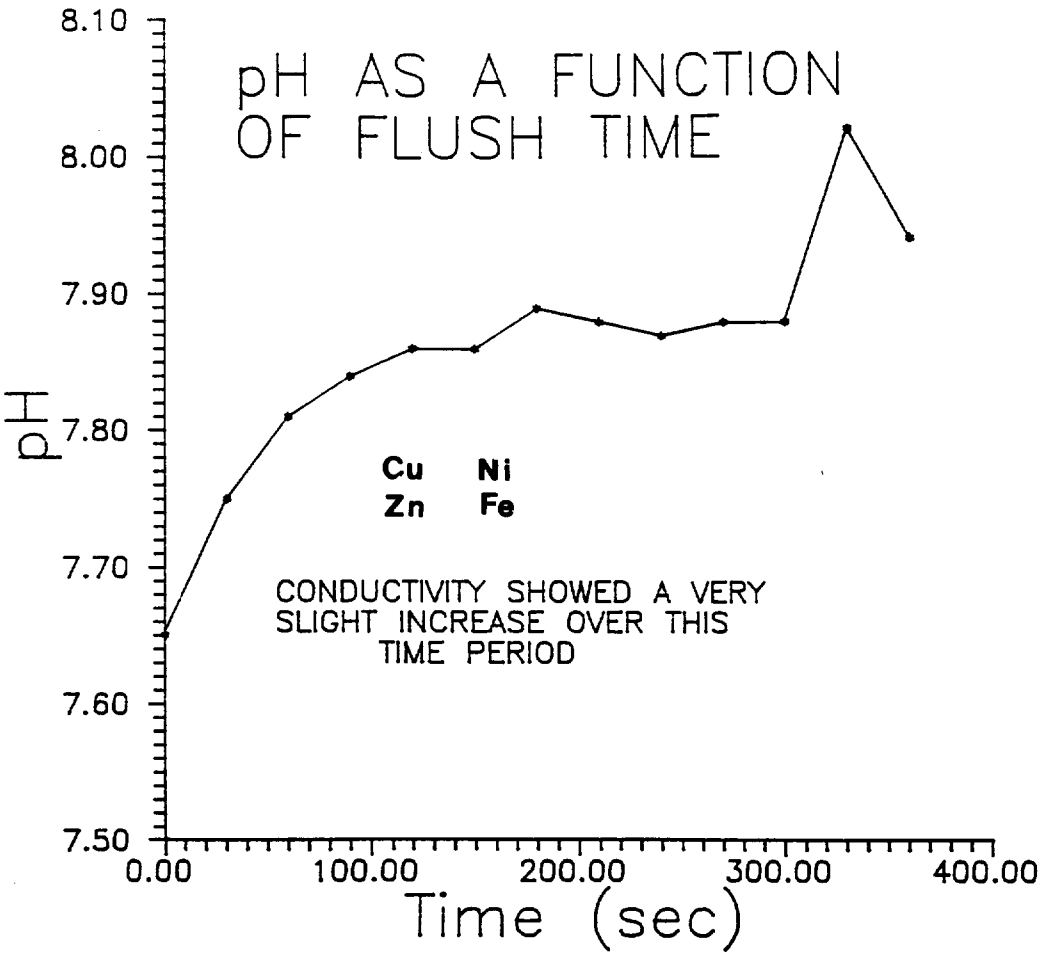
From here the lead dosage can be determined for these particular days and drinks. The average highest dosage of lead per drink at 122ppb was found to be 10.91 ug per drink. The highest maximum dosage was determined by looking at the highest lead level fountain site and the highest drink volume which was reported. This showed the possibility of having a lead dosage as high as 38.41ug per drink.

WORST DOSAGE SCENARIO (122 ppb, Pb)			
Pb DOSAGE	**8.68 μg ± 5.84 μg**	**9.07 μg ± 6.76 μg**	**14.46 μg ± 10.12 μg**
HIGH	**21.18 μg**	**31.52 μg**	**38.41 μg**
LOW	**2.54 μg**	**2.83 μg**	**1.95 μg**

*** THE AVERAGE WORST DOSAGE OF Pb PER DRINK AT 122ppb = 10.91 μg/drink**

****THE WORST MAX WAS AT 38.41 μg/drink**

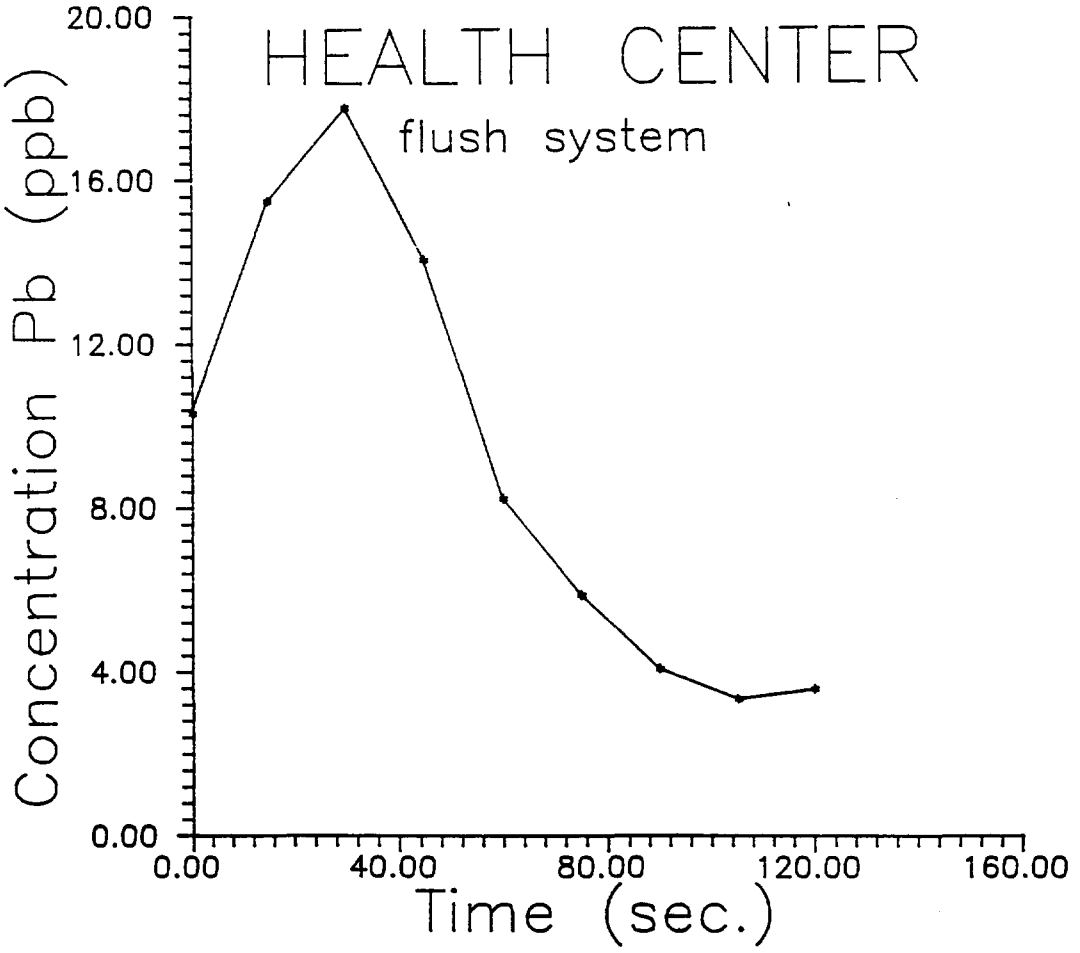
The next step was to look at the Kinetics of the water coolers. This relationship shows the pH as a function of flush time.



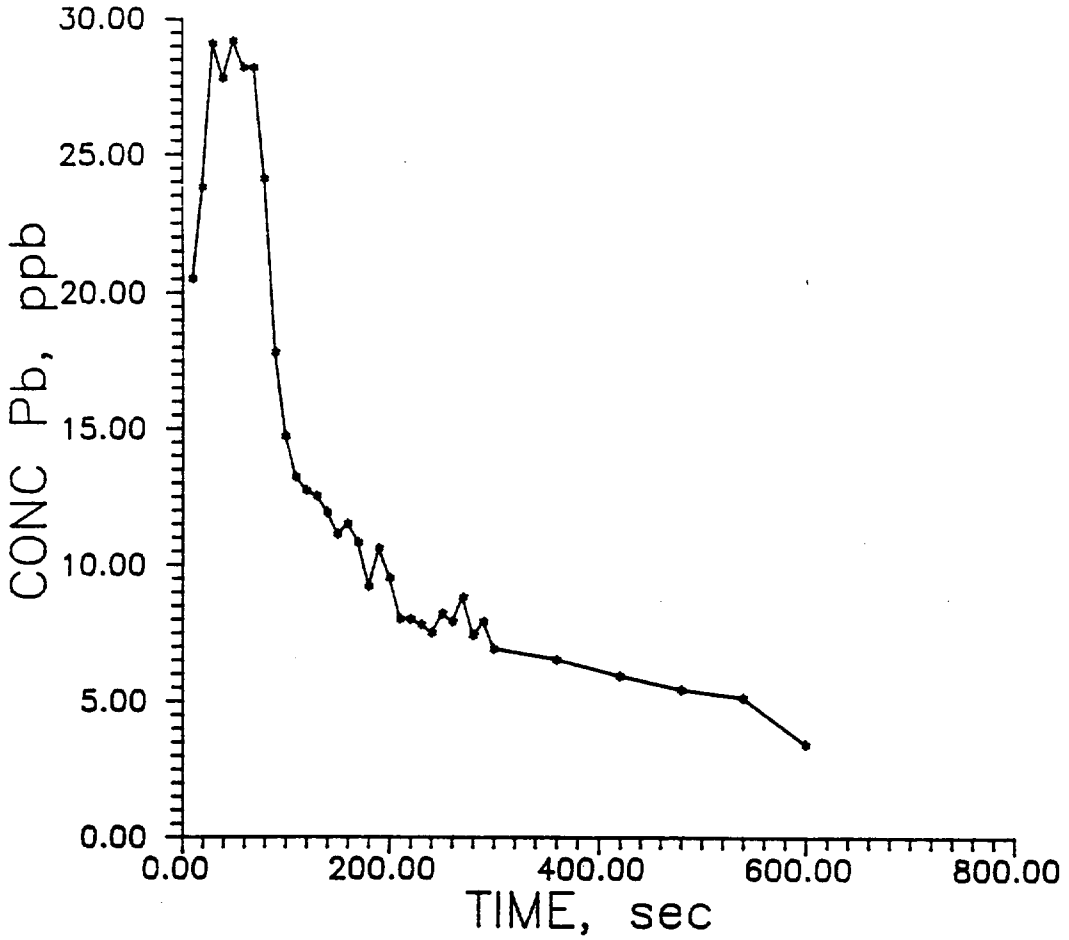
Initially, the pH starts out approximately 7.65 and increases to about 7.85 within two minutes. From here the pH tends to level off. As one can see, conductivity showed a very slight increase over this time period. Since Copper, Iron, Nickel, and Zinc precipitate and form hydroxide, it is possible that this caused the $--OH^-$ to decrease and be leached out. This is not a major change but we do say it is a trend.

Next, we focused on the Kinetics of the lead. By continuously running the fountain for two minutes while carefully taking 10mL

samples every fifteen seconds, the flush kinetics may be determined. This is a typical example of the relationship between lead concentration and time.



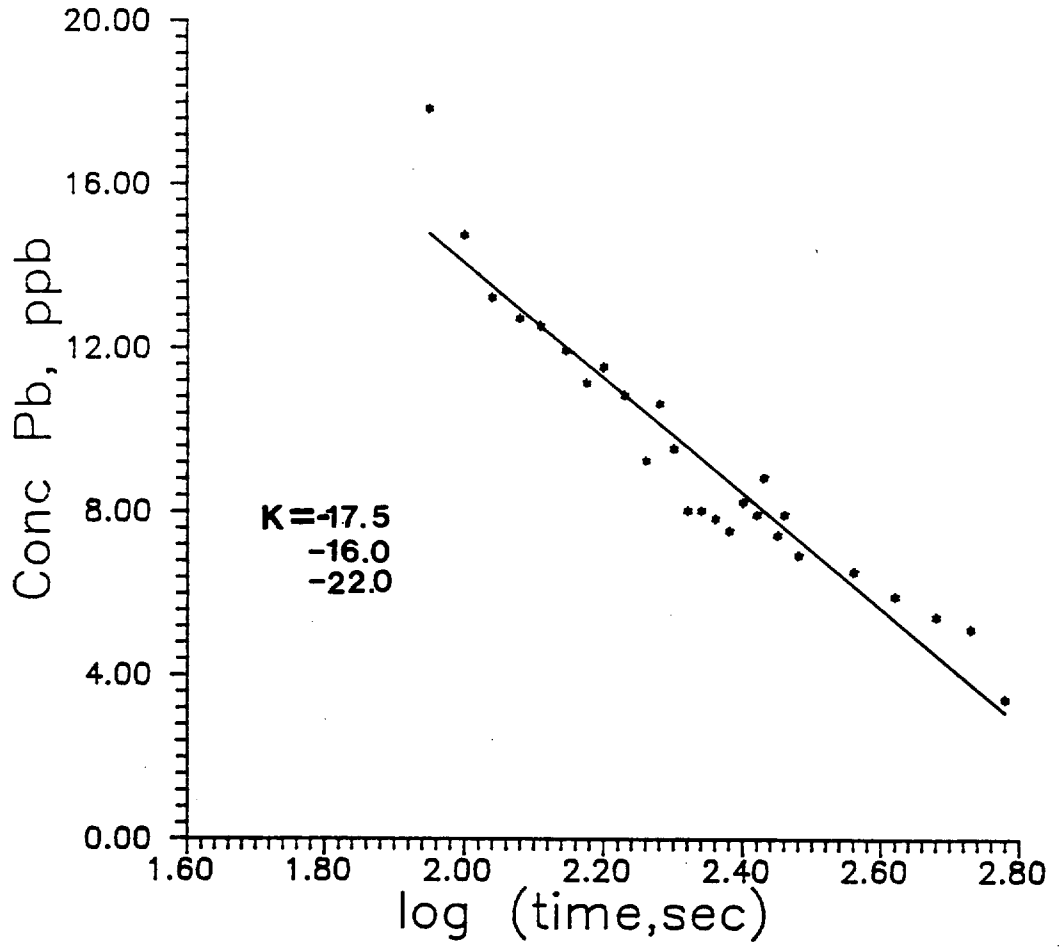
Later, we looked at a more detailed Kinetics study dealing with how the lead leached out of the fountain. In the figure below, the initial concentration of lead was approximately 21ppb. We see a slight increase as the previously sedate water moves through the system.



Then, a very noticeable exponential decline becomes evident as the level drops from 29.5ppb to 3.5 ppb within a ten minute period. Here was a water cooler which could initially have the potential to be dangerous. Nevertheless, after ten minutes of flushing it has decreased to minimal levels.

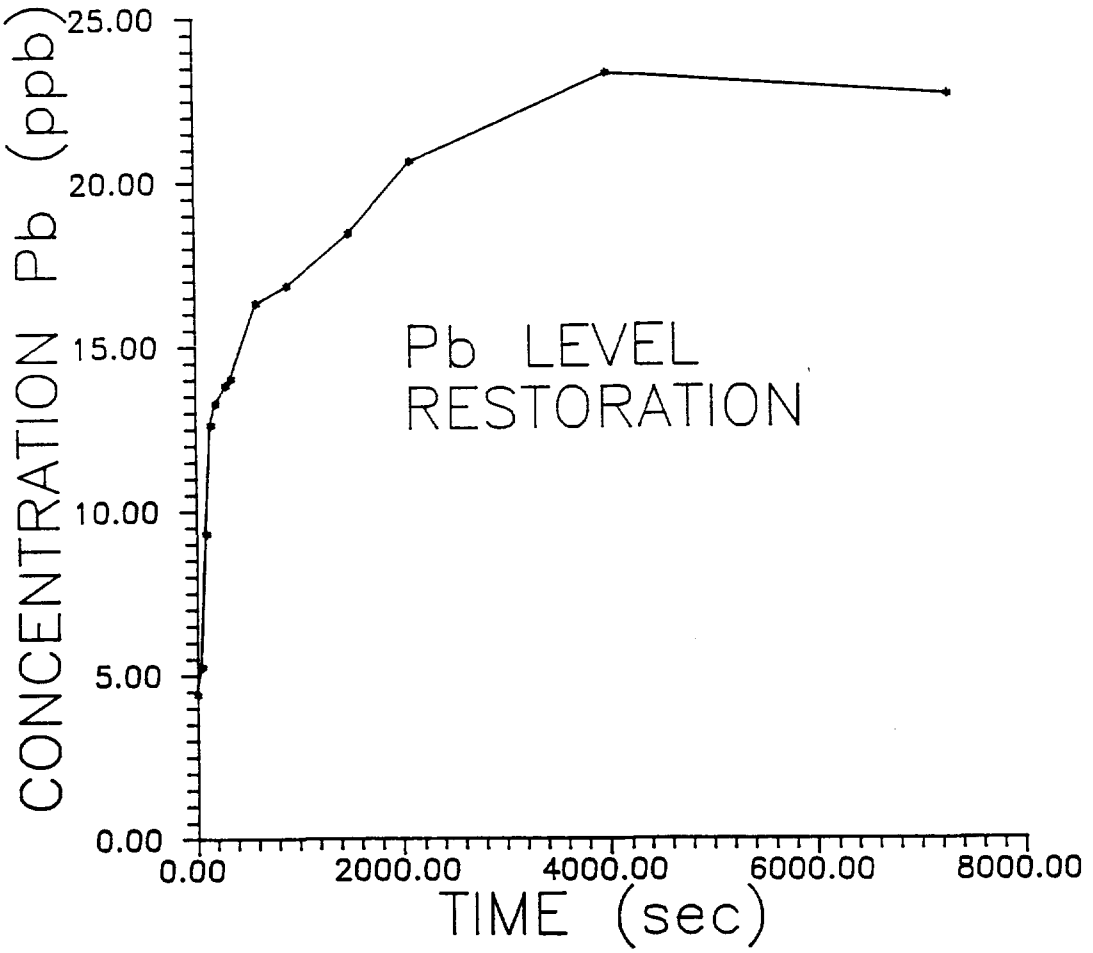
To illustrate the logarithmic relationship, we plotted the log

of the time in seconds versus the concentration of lead in parts per billion. The initial rapid rise was not plotted in order to concentrate on the rate of decay. On this particular regression there is a decay of -17.5. Other similar plots have been found to have decay constants of -16.0 and -22.0.



It is important to note that this relationship does not represent a chemical kinetics test. Instead, it focuses on the kinetics due to the flushing of the water out of the system. However, chemical kinetics does seem to be associated with the restoration of lead levels.

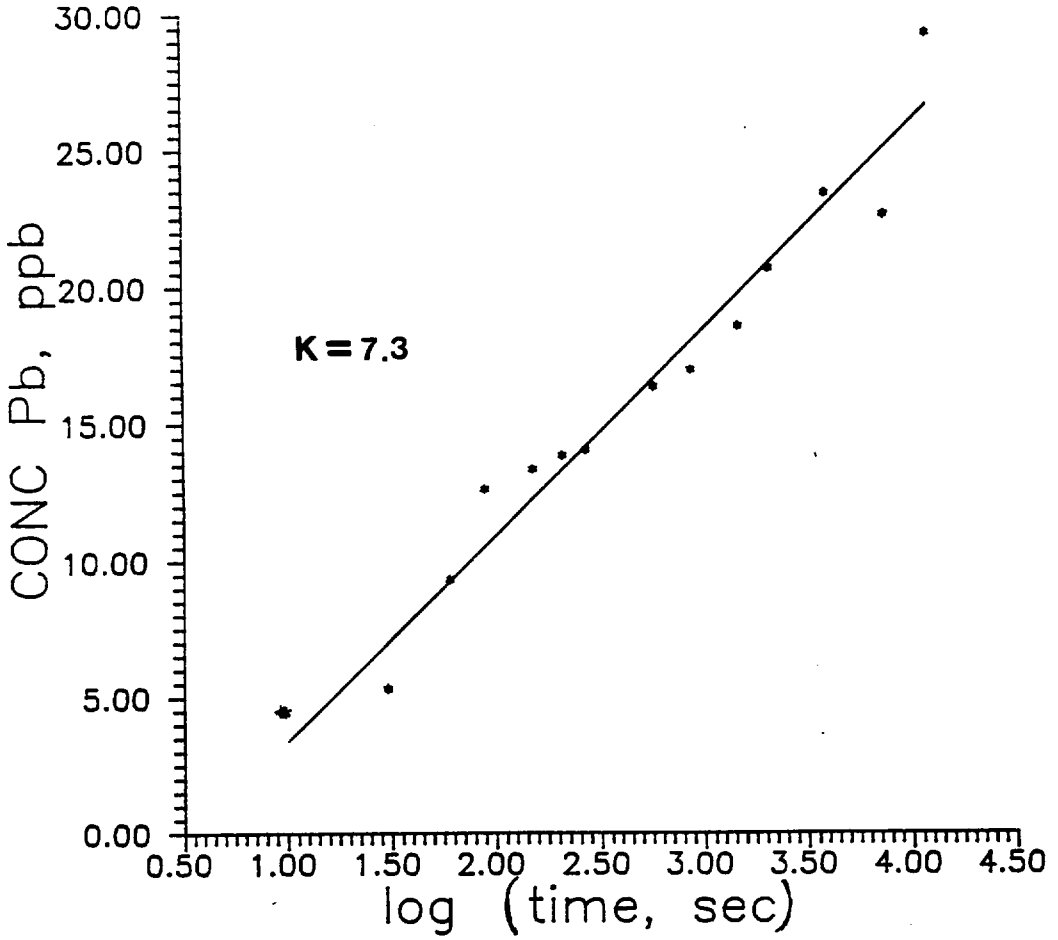
After watching the lead decay, we wanted to see how quickly lead levels could be restored. By taking 10mL samples at varied time intervals and analyzing the data, a rapid rise in lead levels is noted.



Above is a relationship which represents the lead restoration. After flushing, the concentration starts out rather low, but quickly rises to a level of approximately 23ppb, which happens to be comparable to the initial starting point. All of this took place within an hour. In essence, we did not have to wait a whole weekend to generate high levels of lead.

Another example of the logarithmic relationship is shown below. There tends to be some scatter, but overall these results are quite

remarkable. This particular run shows a restoration constant of 7.3 and a similarity to First Order Kinetics.



In conclusion, the growth seems to seems to be one-half of the decline.

To summarize, it is important to note that the water coolers which were tested were the older models. The problem seems to be random throughout the university because the majority of the coolers were found to be below the detection limits. It is still important to note that approximately 1 in 6 coolers fall into the area of concern for replacement. The most potentially dangerous usage of the cooler seems to be the first minute and a half of

flushing. After flushing for approximately ten minutes, the lead levels decrease to minimal levels. Nevertheless, within a few hours the lead levels can restore themselves close to the initial concentration. In essence, it does not take a weekend to restore the potentially toxic lead. Our study concluded that with frequent fountain usage, the level of lead remained below toxic limits. However, the danger lies in the inability to assure frequent usage.

REFERENCES CITED

--- Lansdown, Richard, and William Yule. Lead Toxicity: History and Environmental Impact. Baltimore: The Johns Hopkins UP, 1986.